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Battery separator with improved oxidation stability

The invention relates to separators for lead/sulphuric acid accumulators, hereafter called lead accumulator for short, which have an improved oxidation resistance.

The separators used today in lead accumulators are mostly filled, microporous polyolefin separators. These are intended on the one hand to prevent a direct contact and thus short circuits between the electrode plates, and on the other hand to make possible an ionic current flow and offer this the smallest possible resistance. The composition and production of such separators are known per se (cf. e.g. DE-PS 1 267 423, DE-PS 1 298 712, DE-AS 1 496 123, DE-OS 35 45 615, DE-PS 35 40 718 and DE-PS 36 17 318).

According to US 3 351 495, to this end a homogeneous mixture of polyolefin, filler, plasticizer and additives is formed and this is formed into a web-shaped layer. Then the plasticizer and fillers are at least partly removed by extraction. Polyethylene glycol, glycerin and in particular mineral oil are used as plasticizer. To prevent an oxidative degradation of the polyolefin during extrusion the separators can also contain antioxidants such as 4,4-thio-bis-(6-tert-butyl-m-cresol) and 2,6-di-tert-butyl-4-methylphenol.

When in use the separators must not only resist the aggressive battery acid but are also exposed, particularly in the area of the positive plate, to oxidative attacks, for example by oxidative lead dioxide and the formation of extremely reactive nascent oxygen and peroxides. In addition to this, lead accumulators are exposed to ever higher ambient temperatures and cycle loads, which further intensifies the oxidative attack.

Although the polyethylene frequently used for the production of the separators does give the separators, in combination with small quantities of antioxidant and a larger quantity of oil, a certain oxidation stability vis-à-vis the aggressive medium of the battery, the separator material can still undergo slow oxidative attack under more difficult conditions of use and finally be destroyed, which results in a deterioration of the mechanical stability of the separator and the formation of cracks and holes and which in the most unfavourable case shortens the battery life through short circuits.

Many measures for improving the oxidation stability of battery separators are known. For example, the oxidative

degradation of the separator can be delayed by increasing the separator thickness, the molecular weight of the polymer used to produce the separator or through a significant increase in the polymer content of the separator.

However, an increase in the separator thickness leads to appreciably higher production costs and higher electrical resistances. The ultra-high molecular-weight polyethylene (UHMWPE) customarily used to produce separators also generally already has a molecular weight of $5 - 7 \times 10^6$ g/mol and a further increase in the molecular weight would lead to considerable process problems. Moreover, although UHMWPE types with a molecular weight of up to approximately 10×10^6 g/mol are commercially available, the polymer chains of these UHMWPE types are markedly degraded during extrusion by shearing in the extruder, which again substantially reduces the molecular weight. An increase in the polymer content causes the wettability and porosity and thus the electrical resistance of the separator to deteriorate significantly.

It is also known from the state of the art that the process oils used to produce the battery separators can improve the oxidation resistance of the separators. The maximum oil content of the separators is restricted however, because the oil also causes the wettability and porosity of the separator to deteriorate.

DE 30 04 659 C2 discloses separators which contain oils with an aromatics content of at least 40 %. Because of their composition, these oils bring about an improvement in the oxidation resistance of the separators. However, process oils with a high aromatics content can encourage

the formation of dark, often sticky deposits in the lead accumulator which contaminate the inside and outside of the accumulator case and can block the valve systems.

The prevention of such deposits is the subject-matter of DE 39 22 160 A1, which to this end discloses the use of surfactants, preferably of the amide or amine type.

JP 02155161 A discloses the use of a combination of paraffin oil, antioxidant and a peroxide decomposer based on phosphoric acid to improve the oxidation stability of battery separators at high temperatures. However this does not provide protection against the oxidative effect of nascent oxygen or of the lead dioxide of the positive electrode plate.

JP 07130348 A discloses separators which contain mineral oil in combination with a phenolic resin.

To improve the oxidation stability of pocket separators an increase in the oil content in the fold edge and along the weld edge is proposed in US 5,384,211 and JP 10031992 A.

JP 08203493 A discloses the coating of the edges of separators with an insulating resin in order to suppress the oxidative attack.

JP 2000133239 A describes the coating of the upper part of the separator, which is in contact with the frame and the electrode lug of the positive plate, with a hot-melt adhesive.

The above separators cannot be produced continuously with today's techniques, and the process is thus time-consuming and expensive. Moreover only a partial improvement in oxidation stability is achieved.

It is customary to provide separators with longitudinal ribs on at least one side in order to prevent direct contact of the separator sheet with the positive electrode plate and thus a premature oxidative destruction.

JP 04167356 A and JP 2000182593 A disclose separators which have additional ribs in the area of the weld edges of the separators in order to prevent in a targeted way the formation of cracks through oxidation in this area.

JP 09097601 A discloses separators profiled in a particular way which allow the gas which forms on the positive plate to escape more quickly and are thus intended to reduce its oxidative effect on the separator.

JP 04190554 A describes the addition of glass fibres to the separator material in order to delay a deterioration of the mechanical properties of the separator through oxidation. The introduction of glass fibres into the separator by extrusion is difficult however, because glass fibres on the one hand are dispersible only with difficulty in the separator material and on the other hand break easily during extrusion and block the extruder screens. Also, separators containing glass fibres are not very flexible and tend to break when subjected to a mechanical stress.

Despite considerable efforts, none of the present methods for improving the oxidation resistance of battery separators is completely satisfactory.

Battery separators are known from US 4,024,323 in which at least 40 % of the ultra-high molecular-weight polyethylene used for the production of separators are replaced by a copolymer of an olefin and (meth)acrylic acid or a mixture of a polyolefin of low molecular weight and a polymer of (meth)acrylic acid. This is intended to increase the extrusion speed and improve the incorporation of the filler into the polymer. The replacement of at least 40 % of the ultra-high molecular-weight polyethylene by low-molecular-weight polymers is disadvantageous, however, because it leads to a deterioration of the mechanical properties of the separator.

The object of the invention is to provide battery separators with high oxidation stability which are easy and inexpensive to produce and which are protected over their whole surface against oxidation.

According to the invention this object is achieved by battery separators which contain a compound with the Formula (I)

$$R(OR^1)_n\ (COOM^{x+}{}_{1/x})_m \quad (I)$$

in which

R is a non-aromatic hydrocarbon radical with 10 to 4200 carbon atoms, preferably 13 to 4200, which can be interrupted by oxygen atoms,

R^1 is H, $-(CH_2)_kCOOM^{x+}{}_{1/x}$ or $-(CH_2)_k-SO_3M^{x+}{}_{1/x}$, preferably H, where k is 1 or 2,

M is an alkali metal or alkaline-earth metal ion, H^+ or NH_4^+, where not all the variables M simultaneously have the meaning H^+,

n is 0 or 1,

m is 0 or an integer from 10 to 1400 and

x is 1 or 2,

the ratio of oxygen atoms to carbon atoms in the compound according to Formula (I) being in the range from 1:1.5 to 1:30 and m and n not being able to simultaneously be 0. However, preferably only one of the variables n and m is different from 0.

By non-aromatic hydrocarbon radicals is meant radicals which contain no aromatic groups or which themselves represent one. The hydrocarbon radicals can be interrupted by oxygen atoms, i.e. contain one or more ether groups.

R is preferably a straight-chain or branched aliphatic hydrocarbon radical which can be interrupted by oxygen atoms. Saturated, uncross-linked hydrocarbon radicals are quite particularly preferred.

Surprisingly it was found that through the use of the compounds of Formula (I) for the production of battery separators, they can be effectively protected against oxidative destruction.

Battery separators are preferred which contain a compound according to Formula (I) in which

R is a hydrocarbon radical with 10 to 180, preferably 12 to 75 and quite particularly preferably 14 to 40 carbon atoms, which can be interrupted by 1 to 60, preferably 1 to 20 and quite particularly preferably 1 to 8 oxygen atoms, particularly preferably a hydrocarbon radical of formula $R^2-[(OC_2H_4)_p\ (OC_3H_6)_q]-$, in which

R^2 is an alkyl radical with 10 to 30 carbon atoms, preferably 12 to 25, particularly preferably 14 to 20 carbon atoms,

p is an integer from 0 to 30, preferably 0 to 10, particularly preferably 0 to 4 and

q is an integer from 0 to 30, preferably 0 to 10, particularly preferably 0 to 4,

compounds being particularly preferred in which the sum of p and q is 0 to 10, in particular 0 to 4,

n is 1 and

m is 0.

Formula $R^2-[(OC_2H_4)_p\ (OC_3H_6)_q]-$ is to be understood as also including those compounds in which the sequence of the groups in square brackets differs from that shown. For example according to the invention compounds are suitable in which the radical in brackets is formed by alternating (OC_2H_4) and (OC_3H_6) groups.

Additives in which R^2 is a straight-chain or branched alkyl radical with 10 to 20, preferably 14 to 18 carbon atoms have proved to be particularly advantageous. OC_2H_4 preferably stands for OCH_2CH_2, OC_3H_6 for $OCH(CH_3)CH_2$ and/or $OCH_2CH(CH_3)$.

As preferred additives there may be mentioned in particular alcohols (p=q=0; m=0) primary alcohols being

particularly preferred, fatty alcohol ethoxylates (p=1 to 4, q=0), fatty alcohol propoxylates (p=0; q=1 to 4) and fatty alcohol alkoxylates (p=1 to 2; q=1 to 4) ethoxylates of primary alcohols being preferred. The fatty alcohol alkoxylates are for example accessible through reaction of the corresponding alcohols with ethylene oxide or propylene oxide.

Additives of the type m=0 which are not, or only difficultly, soluble in water and sulphuric acid have proved to be particularly advantageous.

Also preferred are battery separators which contain a compound according to Formula (I), in which

R is an alkane radical with 20 to 4200, preferably 50 to 750 and quite particularly preferably 80 to 225 carbon atoms,

M is an alkali metal or alkaline-earth metal ion, H^+ or NH_4^+, in particular an alkali metal ion such as Li^+, Na^+ and K^+ or H^+, where not all the variables M simultaneously have the meaning H^+,

n is 0,

m is an integer from 10 to 1400 and

x is 1 or 2.

As suitable additives there may be mentioned here in particular polyacrylic acids, polymethacrylic acids and acrylic acid-methacrylic acid copolymers, whose acid groups are at least partly, i.e. preferably 40 %, particularly preferably 80 %, neutralized. The percentage refers to the number of acid groups. Quite particularly preferred are poly(meth)acrylic acids which are present

entirely in the salt form. By poly(meth)acrylic acids are meant polyacrylic acids, polymethacrylic acids and acrylic acid-methacrylic acid copolymers. Poly(meth)acrylic acids are preferred and in particular polyacrylic acids with an average molar mass M_W of 1,000 to 100,000 g/mol, particularly preferably 1,000 to 15,000 g/mol and quite particularly preferably 1,000 to 4,000 g/mol. The molecular weight of the poly(meth)acrylic acid polymers and copolymers is ascertained by measuring the viscosity of a 1 % aqueous solution, neutralized with sodium hydroxide solution, of the polymer (Fikentscher's constant).

Also suitable are copolymers of (meth)acrylic acid, in particular copolymers which, besides (meth)acrylic acid contain ethylene, maleic acid, methyl acrylate, ethyl acrylate, butyl acrylate and/or ethylhexyl acrylate as comonomer. Copolymers are preferred which contain at least 40 wt.-%, preferably at least 80 wt.-% (meth)acrylic acid monomer, the percentages being based on the acid form of the monomers or polymers.

To neutralize the polyacrylic acid polymers and copolymers, alkali metal and alkaline-earth metal hydroxides such as potassium hydroxide and in particular sodium hydroxide are particularly suitable.

Suitable additives according to the invention are known and are commercially available.

As well as the named additives the separators can alternatively or additionally contain compounds which can form the additives according to the invention. Preferred are compounds which, when the separators are used for the intended purpose release suitable additives, for example by hydrolysis with the battery acid. Particularly

suitable substances of this type are esters which form OH-group-containing compounds of Formula (I). These include for example phthalic acid esters of the above-named alcohols.

The battery separators can be provided in various ways with the additive or additives. The additives can for example be applied to the separator when it is finished (i.e. after the extraction) or added to the mixture used to produce the separator. According to a preferred embodiment the additive or a solution of the additive is applied to the surface of the separator. This variant is suitable in particular for the application of non-thermostable additives and additives which are soluble in the solvent used for the subsequent extraction. Particularly suitable as solvents for the additives according to the invention are low-molecular-weight alcohols, such as methanol and ethanol, as well as mixtures of these alcohols with water. The application can take place on the side facing the negative electrode, the side facing the positive electrode or on both sides of the separator. In the case of an application on one side, an application to the side of the separator facing the positive electrode plate is preferred.

The application may also take place by dipping the battery separator in the additive or a solution of the additive and subsequently optionally removing the solvent, e.g. by drying. In this way the application of the additive can be combined for example with the extraction often applied during separator production.

Another preferred option is to mix the additive or additives into the mixture of thermoplastic polymer and optionally fillers and other additives which is used to

produce the battery separators. The additive-containing homogeneous mixture is then formed into a web-shaped material. Because this usually occurs by extrusion at high temperature, difficultly volatile and thermostable additives which are difficultly soluble in the solvent used for extraction, such as polyacrylic acid polymers and copolymers or their salts, are particularly suitable for this.

The additives can be used alone or as a mixture of two or more additives. Mixtures of one or more of the additives according to the invention with surfactants, defoamers and other additives can also be used.

The additives used according to the invention are preferably used in a quantity of 0.5 to 5.0 wt.-% particularly preferably 1.0 to 5.0 wt.-%, quite particularly preferably 1.5 to 4.0 wt.-% and in particular 2.0 to 3.5 wt.-% relative to the mass of the separator after the extraction.

The additives used to produce the separators preferably have a high boiling point. Additives with a boiling point of 250° C or more have proved to be particularly suitable.

The additives used according to the invention are suitable for combining with all separators which are liable to oxidative attacks, in particular for combining with separators based on thermoplastics. Separators which, as well as a thermoplastic, also contain a filler and oil are quite particularly preferred.

Preferably the additives are combined with separators based on polyolefins, particularly preferably filler-containing polyolefins which can be produced by hot-

forming such as extrusion or pressing, and subsequent extraction. The additives are however also suitable for the protection of separators which contain polyolefin threads or fibres, e.g. separators in the form of fleeces.

Preferred polyolefins are polyethylenes, ultra-high molecular-weight polyethylene being particularly preferred according to the invention. Ultra-high molecular-weight polyolefin with an average molecular weight by weight of at least 300,000, preferably at least 1.0×10^6 and particularly preferably at least 5.0×10^6 g/mol is quite particularly preferred.

The molecular weight of the polyethylene is measured by the Margolies equation: $M = 5.37 \times 10^4 [\eta]^{1.49}$; with η = reduced specific viscosity in dl/g (Josef Berzen, CZ Chemie-Technik, 3rd Volume (1974) No. 4, p. 129).

However polypropylene, polybutene, polystyrene, ethylene-propylene copolymers, ethylene-hexylene copolymers, ethylene-butene copolymers, propylene-butene copolymers and ethylene-propylene-butene copolymers are also suitable.

The separators according to the invention preferably contain 10 to 100 wt.-%, particularly preferably 15 to 50 wt.-% and quite particularly preferably 20 to 40 wt.-% polymer, in particular ultra-high molecular-weight polyethylene, relative to the sum of the weights of filler and polymer.

A filler preferred according to the invention is SiO_2, quite particularly preferred fillers are amorphous precipitation silicas. Oxides and hydroxides of silicon, aluminium and titanium as well as mica, talc, silicates

and glass beads are also suitable as fillers. Fillers of this type are disclosed for example in US 3,351,495 and DE 14 96 123 A.

The separators according to the invention preferably contain 0 to 90 wt.-%, particularly preferably 50 to 85 wt.-% and quite particularly preferably 60 to 80 wt.-% filler, relative to the sum of the weights of filler and polymer, silicas preferably being exclusively used as filler.

The weight ratio of filler to polymer is preferably 0 to 9.0, particularly preferably 1.0 to 5.7 and quite particularly preferably 1.5 to 4.0.

Extractable oils which act on the one hand as plasticizers and on the other hand as pore-formers are in particular used as further additives. The liquids disclosed in DE 12 67 423 A, such as for example process oils, are particularly suited. By oils or process oils are preferably meant mineral oils. The oil content in the separator is preferably 5 to 35 wt.-%, particularly preferably 8 to 30 wt.-%, and quite particularly preferably 10 to 25 wt.-% relative to the total mass of the separator after the extraction.

Apart from the main constituents named above, the separators can contain other customary constituents such as carbon black, antioxidants such as for example alkylidene-bisphenols, lubricants, other fillers such as for example talc etc., and optionally also other polymers in more or less secondary quantities. Carbon black is preferably used in a quantity of at most 5 wt.-%, the other additives preferably in a quantity of at most 2 wt.-%, relative in each case to the total mass of the finished separator.

To produce the separators the named materials are carefully mixed in the usual way and then formed into a web-shaped material accompanied by heating. The oil is then extracted from this for example with an organic solvent such as hexane so that the desired porosity is obtained. Finally the separator material is cut to size according to the desired usage form, i.e. preferably cut to the final width, wound up into rolls approximately 1,000 metres in length and packed. The surfaces of the separator can be smooth, ribbed or shaped in any other way. The composition and production of battery separators is sufficiently known from the above-mentioned state of the art. In so far as the additives used according to the invention are soluble in the extraction agent or are able to be extracted with it, they are applied to the separator preferably after the extraction step. The additives can however also be added to the extracting agent and thus be applied to the separator during the extraction.

The separators are mostly used in the form of pockets into which the positive or negative electrode plates are inserted. The pocketed electrode plates are then joined to oppositely-charged non-pocketed electrode plates to form blocks of plates and inserted into a battery container. After filling with sulphuric acid and sealing with a battery block cover the lead accumulator is complete.

The subject-matter of the invention are also lead-sulphuric acid accumulators with at least two oppositely-charged electrode plates which contain at least one battery separator with one of the additives according to the invention.

Apart from the additives used according to the invention the accumulators are customary lead/sulphuric acid accumulators with conventional electrodes and sulphuric acid as electrolyte. Preferably they are starter batteries for motor vehicles. The case can be made of all the customary materials, e.g. polypropylene, hard rubber, acrylic glass, polystyrene, glass etc.

The invention is explained in more detail in the following with reference to embodiments.

Examples

Examples 1 - 7:

Use of 1-dodecanol as additive to prevent premature oxidation of battery separators

Unless stated otherwise battery separators based on polyethylene (UHMWPE) and precipitation silicic acid are used in the examples. The separators are produced on an extruder according to US 3,351,495 and after extrusion are extracted with hexane to an oil content in the base sheet of approximately 12 wt.-% The weight ratio of filler to polymer that is used is given in the respective examples.

In order to assess the effectiveness of the additives a standardized oxidation test was used (PEROX 80 Test) which largely corresponds to the method recommended by the BCI (Battery Council International) for determining the oxidation stability of battery separators (TM-3.229: Standard test method to determine resistance of battery

separator to oxidative degradation using hydrogen peroxide in sulphuric acid as oxidizing medium).

To this end, testpieces from the separator material were treated with a mixture of sulphuric acid and hydrogen peroxide at 80° C for various time periods and the extension of the material before and after the test was compared. The reduction in extendability is a measure of the degradation and the cross-linking, i.e. the oxidative destruction of the polymer. Separators without additives according to the invention which were tested under identical conditions served as comparison.

The testpieces were bone-shaped in accordance with DIN 53455. The oxidation solution was always freshly prepared and consisted of 360 ml sulphuric acid of density 1.28 g/cm^3, 35 ml sulphuric acid of density 1.84 g/cm^3 and 105 ml 35 % hydrogen peroxide solution. The components were slowly mixed with each other accompanied by stirring in the given order and then heated to 80°C in a closed glass vessel in a water bath. Two sample holders each with five testpieces were placed in solution and left in the solution for the desired test period. Then the samples were washed acid free with lukewarm water and the extension was measured. To this end the testpieces were stretched to breaking at a test speed of 300 mm/min. The extension in cross machine direction (CMD) (CMD-expansion) was measured. In each of the following tables the average of ten measured values is given. Because the initial extension of the separators can vary for process reasons, the absolute expansions were normalized to the initial expansion:

$$\frac{\text{absolute stretching after x h Perox Test in \%}}{\text{absolute stretching after 0 h Perox Test in \%}} \times 100 = \text{relative expansion after x h Perox Test}$$

In examples 2 to 7 separator sheets 160 x 300 mm in size were coated on one side with an ethanol solution of 1-dodecanol so that after drying there was 0.7 to 7.1 wt.-% 1-dodecanol on the blade. In the examples, unless stated otherwise, all weight percentages refer to the weight of the separator after extraction. An untreated separator served as comparison (Example 1). In examples 1 to 7 the weight ratio of filler to polymer was 2.6 in each case.

The separators coated with the additive were subjected to the oxidation test described above. After the test had ended the separators coated with 1-dodecanol showed a considerably higher residual expansion than the untreated separator (see Table 1). The results compiled in Table 1 prove that 1-dodecanol, even in extreme test conditions (80°C, H_2O_2) and in small concentrations guarantees improved protection of the separator vis-à-vis oxidative destruction.

Table 1

Oxidation resistance of separators after treatment with 1-dodecanol (oxidation test)

	Example						
	1*)	**2**	**3**	**4**	**5**	**6**	**7**
Quantity of additive	0	0.7	1.4	2.1	2.8	3.5	7.1

[wt.-%]							
Duration of the oxidation test	**Absolute extension [%]**						
0 h	263	269	282	266	271	267	291
20 h	152	186	234	235	233	252	272
40 h	108	156	204	181	197	249	254
72 h	0	46	82	112	135	234	247
	Relative extension [%]						
72 h	0	17	29	42	50	88	85

***)** Comparison example

Example 8:

Study of separators with 1-dodecanol in the battery test

Analogously to Examples 2 to 7 separators were coated with 3.5 wt.-% with 1-dodecanol. The weight ratio of filler to polymer was 2.2, the oil content 12 wt.-% Untreated separators served as comparison. The separators were tested in a lead/sulphuric acid battery. To this end battery cells were assembled from antimony-containing positive plates and negative lead-calcium plates (five positive and four negative plates per cell) with a total capacity of 36 Ah/cell. Three cells were equipped with the dodecanol-coated separators, the other three cells with the untreated separators. The battery was subjected to an intensified stability test at 50° C according to DIN 43539 Part 2 draft 10/1980. Then the cells were opened and the expansion of the separators in the pocket area and in the fold edge was determined.

The results of the battery test are compiled in Table 2. These show that, even under conditions reflecting those encountered in practice, the additive used offers a

noticeable improvement in protection of the separator from oxidative attacks.

Table 2

Oxidation resistance of separators after treatment with 1-dodecanol (battery test)

	Separator without additive*)		**Separator with 3.5 wt.-% 1-dodecanol**	
	before test	after test	before test	after test
Measuring point	**Absolute extension [%]**)**			
in the pocket area	493 ± 42	357 ± 46	513 ± 39	551 ± 49
in the fold edge	493 ± 42	316 ± 24	513 ± 39	429 ± 33
	Relative CMD expansion)**			
in the pocket area	100 %	72 %	100 %	107 %
in the fold edge	100 %	64 %	100 %	84 %

*) Comparison

**) measured after 264 test cycles

Examples 9 -11:

Use of fatty alcohols as additives to prevent premature oxidation of battery separators

Analogously to Examples 1 to 7 separators with alcoholic solutions of 1-tetradecanol, 1-hexadecanol and 1-octadecanol were coated on one side. After drying there was in each case a quantity of 3.5 wt.-% of the additive

on the separator. The separators were subjected to the oxidation test described in Examples 1 to 7. The results are compiled in Table 3.

Separators which are coated with higher-molecular-weight fatty alcohols also show a clearly improved oxidation stability compared with the untreated separator (Example 1).

Table 3

Oxidation resistance of separators after treatment with fatty alcohols
(oxidation test)

	Example			
	6	**9**	**10**	**11**
Additive	1-dodecanol	1-tetradecanol	1-hexadecanol	1-octadecanol
Quantity of additive [wt.-%]	3.5	3.5	3.5	3.5
Duration of the oxidation test	**Absolute extension [%]**			
0 h	267	271	271	268
20 h	252	265	274	265
40 h	249	238	240	238
72 h	234	212	218	201
	Relative extension [%]			
72 h	88	78	80	75

Examples 12 - 14:

Comparison of the antioxidative effect of process oil and dodecanol

It is known from the state of the art that the oxidation resistance of separators can be improved by increasing the level of process oil. In a comparative test the effect of the oil content on the oxidation stability was compared with the effect of the same quantity of an additive according to the invention (1-dodecanol). The results are shown in Table 4. It is to be noted that the additive according to the invention produces a much more noticeable improvement in oxidation resistance. The separators were produced and the test carried out as described in Examples 1 to 7. The weight ratio of filler to polymer was 2.4. In each case the oil was extracted to the content given in the Table.

Table 4

Oxidation resistance of separators after treatment with 1-dodecanol and raising of the oil content (oxidation test)

Example	**12*)**	**13*)**	**14**
Additive	none	none	1-dodecanol (3.5 wt.-%)
Oil content [wt.-%]	12.4	15.4	11.2
Duration of oxidation test	**Absolute extension [%]**		
0 h	407	431	419
20 h	313	370	406
40 h	218	346	388
72 h	99	204	326
96 h	0	77	218
	Relative extension [%]		
96 h	0	18	52

*) Comparison example

Examples 15 - 18:

Use of alkoxylated alcohols as additives to prevent premature oxidation of battery separators

Analogously to examples 1 to 7 separators were treated with alkoxylated alcohols and then subjected to the oxidation test. The weight ratio of filler to polymer was 2.6. Compounds of the general formula $R^2-(OC_2H_4)_p-OH$ were studied, R^2 and p having the meaning given in Table 5. The results compiled in Table 5 show that the addition products of ethylene oxide on long-chain alcohols can noticeably improve the oxidation resistance of battery separators.

Table 5

Oxidation resistance of separators after treatment with fatty alcohol ethoxylates (oxidation test)

	Example					
	1*)	**6**	**15**	**16**	**17**	**18**
Additive: $R^2-(OC_2H_4)_p-OH$						
R^2	C_{12}	C_{12}	C_{12}	$C_{16/18}$	$C_{16/18}$	$C_{16/18}$
p	-	-	2	2	5	11
Quantity of additive [wt.-%]	0	3.5	3.5	3.5	3.5	3.5
Duration of oxidation test	**Absolute expansion [%]**					
0 h	263	267	281	292	279	284
20 h	152	252	246	242	279	257
40 h	108	249	224	260	227	234
72 h	0	234	145	212	159	84
	Relative expansion [%]					

72 h	0	88	52	73	57	30

*) Comparison example

Example 19:

Use of phthalic acid esters as additives to prevent premature oxidation of battery separators

Analogously to Examples 1 to 7 separators were prepared and their oil content was set at 12 wt.-% by extraction with hexane. The weight ratio of filler to polymer was 2.2. Differently from Examples 1 to 7, 1 or 2 wt.-% stearyl phthalate was added to the hexane bath for the treatment of the separators according to the invention. The separators were removed from the bath following the extraction and dried at room temperature after dripping. After drying the separators contained 1 or 2 wt.-% stearyl phthalate. According to Table 6 an effective protection of the separator against premature oxidation is achieved by stearyl phthalate. Stearyl phthalate is split by the battery acid into phthalic acid and octadeanol, an additive suitable according to the invention.

Table 6

Oxidation resistance of separators after treatment with stearyl phthalate (oxidation test)

Additive	**none**	**Stearyl phthalate**	
		1 wt.-%	2 wt.-%
Duration of oxidation test	**Absolute extension [%]**		
0 h	498	498	512
72 h	78	211	251

	Relative extension [%]		
72 h	16	42	49

Examples 20 - 26:

Use of polyacrylates as additives to prevent premature oxidation of battery separators

Analogously to Examples 1 to 7 battery separators with a weight ratio of filler to polymer of 2.2 were prepared based on polyethylene (UHMWPE) and amorphous silicon dioxide. Differently from Examples 1 to 7, polyacrylic acid or the sodium salt of polyacrylic acid were added to the separator material before extrusion, the quantities of polyacrylic acid present in the separator after extraction being given in Table 7. The separators were then subjected to the oxidation test. The results compiled in Table 7 show that salts of polyacrylic acid give an effective protection of the separators against premature oxidation possible. In contrast to this, free polyacrylic acid was practically without effect. The results also show that polyacrylic acids are not washed out of the separator during extraction.

Table 7

Oxidation resistance of separators with polyacrylic acid (oxidation test)

Example	**20*)**	**21**	**22**	**23**	**24**	**25**	**26*)**
Additive	none	Polyacrylic acid					
Average molecular weight [g/mol]	--	1,200	4,000	8,000	15,000	30,000	100,000
Form	--	salt**)	salt**)	salt**)	salt**)	salt**)	acid
K-value ***)	--	15	25	30	40	50	80

Concentration [wt.-%]	--	2.0	2.0	2.0	2.0	2.0	2.0
Duration of oxidation test	**Absolute extension [%]**						
0 h	508	522	468	530	499	504	447
20 h	420	446	413	410	456	485	418
40 h	303	427	394	413	450	457	211
72 h	21	333	273	240	244	224	16
	Relative extension [%]						
72 h	4	64	58	45	49	44	4

*) Comparison example

**) The sodium salt of polyacrylic acid was used (completely neutralized form)

***) Fikentscher's constant, measured in a 1-% aqueous solution neutralized with sodium hydroxide solution, parameter for characterization of the degree of polymerization and the molar mass

Examples 27 - 28:

Use of polyacrylic acid copolymers as additives to prevent premature oxidation of battery separators

Analogously to Examples 20 to 26 separators were prepared and tested which contained polyacrylic acid copolymers instead of polyacrylic acid. In Example 27 the polymer Sokolan CP 10 was used, in Example 28 Sokolan CP 10 S (both Fa. BASF, Ludwigshafen). The results are shown in Table 8. Here also the salt form of the polymers produces a good oxidation protection while the acid form is practically without effect.

Table 8

Oxidation resistance of separators with polyacrylic acid copolymers

(oxidation test)

Example	**23*)**	**27**	**28**
Additive	**none**	**Polyacrylic acid copolymer**	
Average molecular weight [g/mol]	--	4,000	4,000
Form	--	salt**)	acid
Concentration [wt.-%]	--	2.0	2.0
Duration of oxidation test	**Absolute extension [%]**		
0 h	508	521	556
20 h	420	465	506
40 h	303	433	375
72 h	21	279	43
	Relative extension [%]		
72 h	4	54	8

*) Comparison example

**) The sodium salt of polyacrylic acid was used (completely neutralized form)